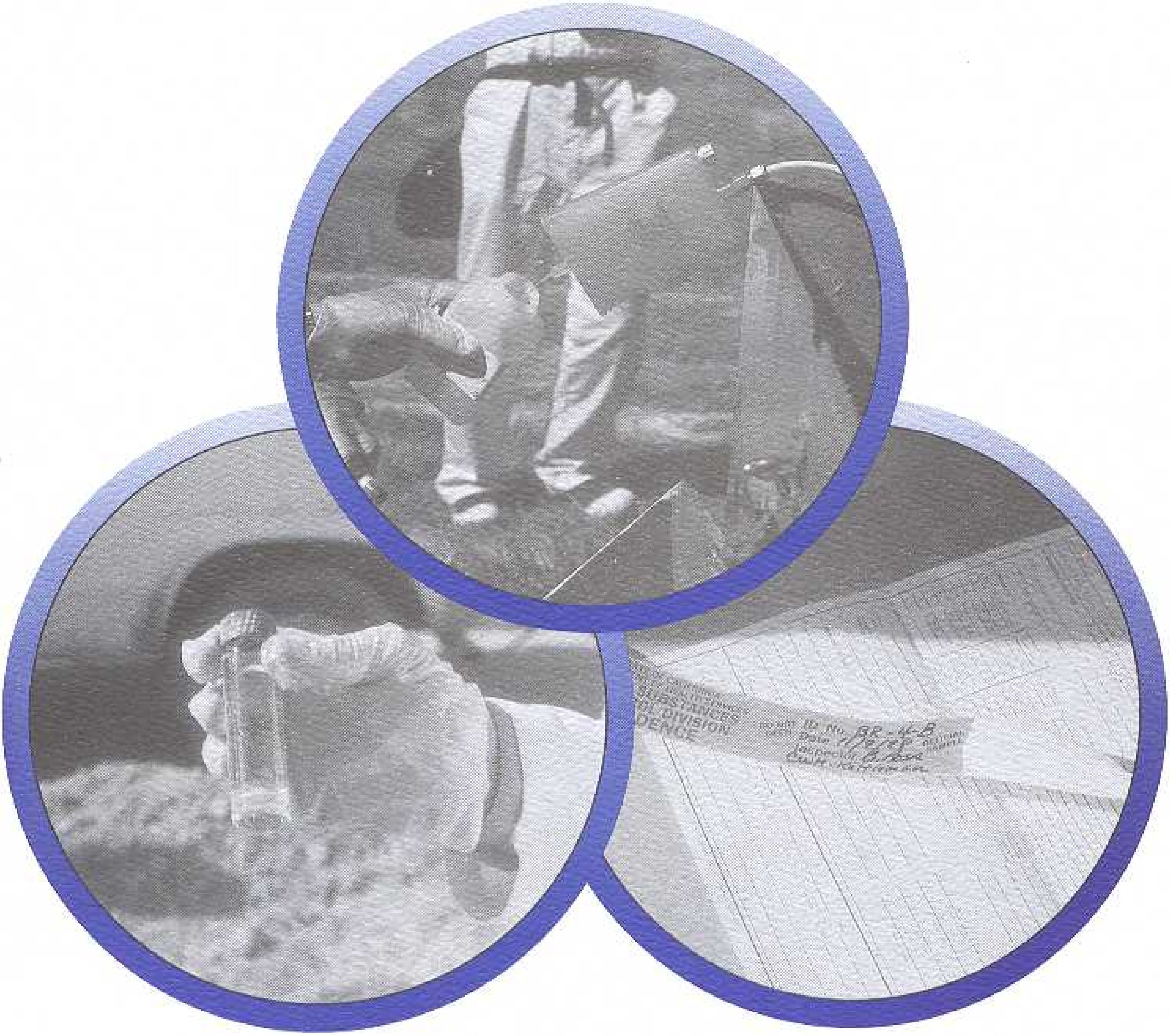
Representative Sampling of Ground Water for Hazardous Substances

Guidance Manual for Ground Water Investigations



State of California
Environmental Protection Agency

REPRESENTATIVE SAMPLING OF GROUND WATER FOR HAZARDOUS SUBSTANCES

Guidance Manual for Ground Water Investigations

July 1995

Pete Wilson
Governor
State of California

James Strock
Secretary
California Environmental Protection Agency

The California Environmental Protection Agency:

Department of Toxic Substances Control
State Water Resources Control Board
Integrated Waste Management Board
Air Resources Board
Department of Pesticide Regulation
Office of Environmental Health Hazard Assessment

FOREWORD

The California Environmental Protection Agency (Cal/EPA) is charged with the responsibility of protecting the state's environment. Within Cal/EPA, the Department of Toxic Substances Control (DTSC) has the responsibility of managing the state's hazardous waste program to protect public health and the environment. The State Water Resources Control Board and the nine Regional Water Quality Control Boards (RWQCBs), also part of Cal/EPA, have the responsibility for coordination and control of water quality, including the protection of the beneficial uses of the waters of the state. Therefore, the RWQCBs work closely with DTSC in protecting the environment.

To aid in characterizing and remediating hazardous substance release sites, Cal/EPA had established a technical guidance work group to oversee the development of guidance documents and recommended procedures for use by its staff, local governmental agencies, responsible parties and their contractors. The Geological Support Unit (GSU) within Cal/EPA provides geologic assistance, training and guidance. This document was prepared by GSU staff in cooperation with the technical guidance work group and the RWQCBs. This document provides guidelines for the investigation, monitoring and remediation of hazardous substance release sites. It should be used in conjunction with the two-volume companion reference for hydrogeologic characterization activities:

> ***Guidelines for Hydrogeologic Characterization of Hazardous Substances Release Sites***
> ***Volume I: Field Investigation Manual***
> ***Volume 2: Project Management Manual***

Please note that, within the document, the more commonly used terms, ***hazardous waste site*** and ***toxic waste site,*** are used synonymously with the term hazardous substance release site. However, it should be noted that any unauthorized release of a substance, hazardous or not, that degrades or threatens to degrade water quality may require corrective action to protect its beneficial use.

This document supersedes the 1990 draft of the DTSC ***Scientific and Technical Standards for Hazardous Waste Sites, Volume I, Chapter 9*** and is one in a series of Cal/EPA guidance documents pertaining to the remediation of hazardous substances release sites.

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Marie McCrink	Hazardous Substances Engineering Geologist,
Bill Owen	Hazardous Substances Engineering Geologist,
John Woodling	Senior Hazardous Substances Engineering Geologist.

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1 INTRODUCTION

The guidelines that follow are modified from the 1991 final draft of Test Methods for Evaluating Solid Wac, Volume 11, Chapter 11, published by the United States Environmental Protection Agency (U.S. EPA, 1991). This document is commonly referenced by its document number, **SW-846.** The Department of Toxic Substances Control (Cal/EPA) has incorporated appropriate sections of **SW-846** into this document, in an effort to minimize redundant or contradictory guidance between the California Environmental Protection Agency (Cal/EPA) and U.S. EPA.

Although developed for monitoring and corrective actions at permitted facilities under the Resource Conservation and Recovery Act (RCRA), the methods and materials discussed in Chapter 11 of **SW-846** are applicable to **all** hazardous waste sites. As such, **SW-846** is readily adaptable for investigations pursued under the authority of the Cal/EPA Site Mitigation Program.

1.1 Purpose

This document is intended to provide guidelines for the sampling and analysis of ground water used for the characterization of hazardous waste sites. The purpose of this document is to aid in the selection of sampling devices and analytical methods, provide recommended quality assurance and quality control (QA/QC) procedures, and give a standardized approach to the presentation of the resulting data. The recommendations contained herein represent minimum criteria judged necessary to obtain quality data and assure reasonable and independently verifiable interpretations.

The recommendations presented here are a subset of the larger site characterization process. Refer to the Guidelines for Hvdrogeologic Characterization for Hazardous Substance Release Sites (Cal/EPA, 1995) for additional information on investigative tools.

1.2 Limitations

The recommendations presented here represent the minimum criteria that can aid obtaining quality data and assuring reasonable and independently verifiable interpretations. Some sites may require investigative efforts above and beyond the scope of this document, while at other sites a less rigorous application of this guidance may be appropriate. It is the obligation of the responsible parties and the qualified professionals performing site investigations to consult with pertinent regulatory agencies, identify all requirements and meet them appropriately.

This document discusses broad categories of methods and devices that can be used in the sampling and analysis of ground water. It does not define specific operating procedures for sampling and analysis. Nor does this document propose guidelines for every available sampling device or analytical method. The qualified professional in charge of the field investigation should specify the methods, equipment and operating procedures in an appropriate work plan and document any significant departures from the work plan that were necessary during the course of the investigation.

This document does not supersede existing statutes and regulations. Federal, state and local regulations, statutes, and ordinances should be identified when required by law, and site characterization activities should be performed in accordance with the most stringent of these requirements where applicable, relevant and appropriate.

2 SAMPLING AND ANALYSIS

All procedures and techniques used for site characterization, ground-water monitoring well installation and development, sample collection, sample preservation and shipment, analytical procedures, and chain-of-custody control should be specified in a Sampling and Analysis Plan (SAP). RPs and field personnel should follow the SAP while performing the site characterization, installing and developing monitoring wells, and collecting and analyzing ground-water samples. A description of dates anticipated for initiation, milestones, and completion of project and monitoring activities should be provided. A milestone table or a bar chart consisting of project tasks and time lines is appropriate for inclusion in the SAP.

2.1 Elements of Sampling and Analysis Programs

The SAP consists of a Field Sampling Plan (FSP) and a Quality Assurance Project Plan (QAPP). At a minimum, the SAP should include information on:

- Sampling objectives;
- Pre-sampling activities;
- Sample collection;
- In-situ or field analyses;
- Sample preservation and handling;
- Chain-of-custody control and records management;
- Analytical procedures and quantitation limits for both laboratory and field methods;
- Field and laboratory quality assurance/quality control;
- Evaluation of data quality; and
- Health and safety plan.

The SAP should also include procedures for conducting the site characterization, installing and developing ground-water monitoring wells, and implementing other monitoring programs (e.g., vadose zone monitoring and monitoring of springs).

2.2 Pre-Sampling Activities

2.2.1 Measurement of Static Water Level Elevation

The SAP should include provisions for measuring the static water elevation in each well and the depth of each well prior to each sampling event. Measurement of water level elevations on a continuing basis is important to determine whether horizontal and vertical components of the hydraulic gradient have changed since initial site characterization. A change in ground-water flow may necessitate modification to the design of the ground-water monitoring system. Water level elevations have been measured using a number of devices and methods, including the following:

- Steel tape coated with carpenter's chalk (wetted-tape method);
- Float-type devices;
- Pressure transducers; and
- Electric water level sounders.

These devices and methods are described in more detail in Aller et al. (1989), U.S. EPA (1987), and Nielsen (1991). Nielsen (1991) provides the water level measurement accuracy of each of these devices. The SAP should specify the device to be used for water level measurements, as well as the procedure for measuring water levels.

Regardless of the method or device chosen to measure the water level elevation in a monitoring well or piezometer, the following criteria should be met when determining water level elevations:

- After well construction and development, water levels in piezometers and wells should be allowed to stabilize for a minimum of 24 hours prior to measurement. In low yield aquifers, recovery may take longer, and several water level measurements should be made over a period of several days to ensure that recovery has occurred.
- Water levels (depth to standing water) should be accurately measured with a precision of fO.O1 foot. Water levels should be measured from the survey datum on the top of the inner well casing. The method or device used to measure water levels should be sufficiently sensitive so that a measurement to 0.01 foot can be obtained reliably. In general, the wetted-tape method is the only method for water level measurement that consistently has an accuracy of 0.01 foot (Nielsen, 1991).
- Water level measurements from boreholes, piezometers, or monitoring wells used to define the water table or a single potentiometric surface should be collected within less than 24 hours. This practice is adequate if the magnitude of change is small over that period of time. In certain situations, water level measurements should be made within a shorter time interval. These situations typically include:

  (1) tidally influenced aquifers;

  .(2) aquifers affected by river stage, bank storage, impoundments, and/or unlined ditches;

(3) aquifers stressed by intermittent pumping of production, irrigation or supply wells;

(4) aquifers being actively recharged because of recent precipitation; and

(5) confined or semi-confined aquifers that demonstrate significant water level fluctuations in response to barometric pressure changes.

- Water level and well depth measurement equipment should be constructed of materials that are chemically inert and not prone to sorption.

- Water level and well depth measurement equipment should be decontaminated prior to use at each well to ensure sample integrity and to prevent cross-contamination of ground water.

- Measuring tapes and marked cables that are used to measure water levels and well depths should be periodically calibrated.

- Well depth measurements should be made each time ground water is sampled using a weighted tape measure or marked cable. The weight should be heavy enough to keep the tape measure straight and it should be blunt so that it will not penetrate soft materials on the bottom of the well. The deeper the well, the heavier the weight has to be to "feel" the bottom of the well. Standing water level measuring devices are not appropriate for making well depth measurements.

2.2.2 Detection of Immiscible Layers

The SAP should include provisions for detecting and measuring the thicknesses of immiscible liquid contaminants (i.e., light non-aqueous phase liquids [LNAPLs] and dense non-aqueous phase liquids [DNAPLs]) each time water level is measured if immiscible contaminants are known to occur, or could plausibly occur, in the subsurface at the facility. LNAPLs (also known as "floaters") are relatively insoluble organic liquids, less dense than water, that tend to spread across the water table (in unconfined aquifers). DNAPLs, also known as "sinkers", are relatively insoluble organic liquids that are more dense than water; DNAPLs tend to migrate downward and accumulate on underlying confining layers. The detection of immiscible layers requires specialized equipment that should be used before a well is evacuated for conventional sampling. The SAP should specify the devices to be used to detect LNAPLs and DNAPLs, as well as the procedures to be used for detecting and sampling these contaminants.

LNAPL Detection Collection

RPs should specify in the SAP the following procedures for detecting the presence of LNAPLs. These procedures should be followed before the well is evacuated for conventional sampling:

1. Remove the locking and protective caps.

2. Sample the air in the well head for organic vapors using either a photoionization detector or an organic vapor analyzer, and record measurements.

3. Gently lower a clear disposable bailer into the well to just below the fluid level and retrieve a sample. Use of a clear bailer is best for visually determining the presence of very thin or sheen-type layers.

4. If a measurable thickness of floating product is detected, lower an interface gauging probe or a weighted tape coated with commercially available reactive indicator paste into the well to determine the depth to the air/LNAPL and the LNAPL/water interfaces.

The air above the well head should be monitored to determine the potential for fire, explosion, or health and safety hazards. Air monitoring also serves as a first indication of the presence of LNAPLs. The presence of LNAPLs precludes the exclusive use of water level sounders to make a determination of static water level.

The interface probe serves two related purposes. First, as it is lowered into the well, the probe registers when it is exposed to an organic liquid and thus identifies the presence of LNAPLs. Secondly, after passing through the LNAPL layer, the probe indicates the depth to water. Careful recording of the depths of the air/LNAPL and LNAPL/water interfaces establishes a measurement of the thickness of the LNAPL in the well casing. Extra health and safety precautions should be taken when LNAPLs or DNAPLs are expected in a well, and the lead regulatory agency should be notified when they are detected.

The approach to collecting LNAPL samples depends on the depth to the floating layer surface and the thickness of the layer. A sample of the LNAPL should be collected prior to well purging. To collect an LNAPL sample, a bottom valve bailer is the equipment of choice. The bailer should be lowered slowly until contact is made with the surface of the LNAPL. The bailer should then be lowered to a depth less than that of the LNAPL/water interface depth, determined beforehand using the interface probe.

DNAPL Detection/Collection

RPs should specify in the SAP the following procedures for detecting the presence of DNAPLs. These procedures should be followed before the well is evacuated for conventional sampling:

1. Remove the locking and protective caps.

2. Sample the air in the well head for organic vapors using either a photoionization detector or an organic vapor analyzer, and record measurements.

3. Determine the static ground-water level using a water level sounder or other device listed in Section 2.2.1.

4. Two possible methods to determine the presence of DNAPL are: 1) lower an interface probe (conductivity or resistivity sensor) to the well bottom to determine if an organic liquid is present; or 2) lower a transparent, double check-valve bailer to the bottom of the well and withdraw a sample to visually check for the presence of DNAPL.

The best method for collecting DNAPLs is to use a double-check valve bailer. DNAPLs should be sampled prior to well purging. The key to sample collection is controlled, slow lowering (and raising) of the bailer within the well.

2.2.3 Well Purging

Because the water standing in a well prior to sampling may not be representative of in-situ ground-water quality, the standing water should be purged from the well and filter pack prior to sampling. The SAP should include detailed, step-by-step procedures for purging wells, including the number of well volumes (casing and filter pack) to be removed prior to each sampling event, and the parameters that will be monitored during purging. The equipment to be used for well purging should also be described in the SAP. Purging should generally be performed by pumping water from the well, but in some cases it may be necessary to purge the well by bailing.

The purging procedure should ensure that samples collected from the well are representative of the ground water to be monitored. Two primary criteria are typically used to determine if wells have been purged sufficiently to produce representative ground-water samples. Some investigators believe that the removal of a set number of casing and filter pack volumes, usually between 3 and 10, will yield representative ground-water samples. Other investigators argue that representative samples are obtained (particularly when VOCs are the analytes of interest) when values for certain parameters, usually temperature, pH, dissolved oxygen, turbidity, and specific conductance, have stabilized (e.g., are reproducible within 10 percent). At some sites, these parameters may stabilize at slow rates, which would likely result in the withdrawal of too much water from the well. The opposite result, of removing too little water, is of concern when using the fixed casing volume criterion. Both criteria for indicating sufficient purging are irrelevant when applied to low yielding formations that are incapable of yielding three casing and filter pack volumes before the well goes dry. Most reports on low-yielding wells recommend purging them to dryness and obtaining the sample after water levels have recovered sufficiently to allow collection of the required sample volume, a recommendation with which Cal/EPA agrees.

For most wells, Cal/EPA recommends that a minimum of 3 casing volumes of water (determined from the total column of water in the well) be removed during purging. An acceptable alternate method for purging wells is to pack off the well screen and purge only from the screened interval (in this case, casing volumes are calculated from the pumped interval only). Cal/EPA does not recommend a maximum number of casing volumes for purging. Purging should continue until measurements of temperature, pH, specific conductivity and dissolved oxygen have stabilized. The actual number of casing and filter pack volumes to be removed, and the rate that they should be removed should be determined on a well-by-well basis, depending on both the hydraulic properties of the monitored zone and the hydraulic performance of the well (Barcelona et al., 1990; Barcelona, 1985b).

For wells that are shallow or screened at the water table in high yield formations, purging should draw the water from the uppermost part of the water column to ensure that fresh water from the formation will move upward in the screen. Generally, the well should be purged by placing the pump intake at the air/water interface. This will ensure that all of the water in the casing and filter pack is purged, and it will minimize the possibility of mixing. The same effect can be achieved with a bailer that is lowered just below the water level and then withdrawn.

For wells screened considerably below the water level in medium to high-yielding formations with a large amount of water present in the casing, a packer placed just above the screened section, with a pump placed at the top of, or in the screened area can yield representative water samples in a shorter period of time. This method may save money in the long run, by eliminating the need to containerize and treat the large volumes of water that would accumulate from purging casing volumes relative to the total water column, instead of only the screened section of the well.

The following additional recommendations and requirements also apply to the purging of monitoring wells:

- Wells should be purged at rates below those used to develop the well to prevent further development of the well, to prevent damage to the well, and to avoid disturbing accumulated corrosion or reaction products in the well (Puls et al., 1990; Puls and Barcelona, 1989a; Puls and Barcelona, 1989b; Barcelona, 1985b). A low purge rate will also reduce the possibility of stripping VOCs from the water, and will reduce the likelihood of mobilizing solids in the subsurface that are immobile under natural flow conditions.

- Ground water should be monitored for temperature, specific conductance, and pH at regular intervals during purging, and preceding and subsequent to sampling. Ground water should also be monitored for dissolved oxygen content at regular intervals during purging, and preceding and subsequent to sampling (Puls and Eychaner, 1990; Puls et al., 1990; Puls and Barcelona, 1989a; Puls and Barcelona, 1989b). A flow-through cell should be used for the analysis of temperature, specific conductance, pH and dissolved oxygen. Turbidity measurements may be used by the RP to evaluate the need to redevelop monitoring wells.

- As soon as a well recovers sufficiently after purging, the first sample should be tested for dissolved oxygen and turbidity. Samples should then be collected and placed in containers in order of decreasing sensitivity to volatilization and/or sensitivity to oxidation/reduction reactions. The well should be retested for dissolved oxygen and turbidity after sampling as a measure of purging efficiency and as a check on the stability of the water samples over time.

- A well purged to dryness should be sampled as soon as a sufficient volume of ground water has entered the well to enable the collection of the necessary ground-water samples.

- The RP should ensure that purging does not cause formation water to cascade down the sides of the well screen (this may occur when the water level in the well is lowered into or below the screened interval). At no time should a well be purged to dryness if recharge causes formation water to cascade down the sides of the screen, as this may cause an accelerated loss of volatile constituents, resulting in a sample not representative of actual ground-water quality. This problem should be anticipated; water should be purged from the well at a rate that does not cause recharge water to be excessively agitated. Laboratory experiments have shown that unless cascading is prevented, up to 70 percent of the volatiles present could be lost before sampling.

- If the purged water is contaminated, based on prior test results, the water should be stored in appropriate containers until analytical results are available, at which time proper arrangements for disposal or treatment should be made (i.e., contaminated purge water may be a hazardous waste). Purge water from new wells, for which there are no prior chemical data, should be containerized and assumed potentially contaminated until sample analytical results prove otherwise.

2.2.4 Frequency of Sampling

Sampling frequency, in nearly all cases, should be based on the hydrogeology of the site. There is no maximum sampling frequency set by Cal/EPA. Ground-water analytical results should be reviewed periodically, and sampling frequency modified according to data needs, historical water quality trends and regulatory goals. Cal/EPA recommends a minimum of quarterly sampling for at least the first year of monitoring. To track potential seasonal changes in concentration, at least two sampling rounds should roughly coincide with maximum and minimum water table or potentiometric surface elevations. EPA's guidance document "Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities," Interim Final Guidance (EPA/530-SW-89-026, NTIS PB-89-151-047; U.S. EPA 1989a) suggests a method for choosing a sampling interval that will reflect site-specific hydrogeologic conditions. The method uses the Darcy equation to determine the horizontal component of the average linear velocity of ground water for confined, semi-confined, and unconfined aquifers. This value is used to determine a sampling interval that will yield an independent sample of ground water in diffuse flow regimes.

Recent research performed in the area of ground-water sampling frequency (Barcelona et al., 1989) indicates that ground-water monitoring data should be carefully collected over long periods of time (i.e., greater than two years) to determine optimal sampling frequency and to delineate seasonal trends in ground-water monitoring results. In Barcelona et al.'s study, ground water was collected biweekly for 18 months and analyzed for 26 water quality and geochemical constituents. The researchers determined that for the study site, ground-water sampling performed four to six times per year would result in an estimated information loss below 20% and would minimize redundancy. The researchers concluded that by using careful sampling and analytical procedures, sampling and analytical errors can be controlled to approximately ±20% of the annual mean inorganic chemical constituent concentration in ground water.

2.3 Ground-Water Sampling Equipment Selection and Use

There are three broad categories of ground-water sampling devices: grab samplers (e.g., bailers and syringe devices), positive displacement pumps (e.g., gear drive pump, bladder pump, helical rotor pump, piston pump, centrifugal pump), and suction lift pumps (e.g., peristaltic pump.), (Pohlmann and Hess, 1988 and Nielsen, 1991). Gas contact pumps are also available (Pohlmann and Hess, 1988). Table 1 is a useful guide for selecting devices for sampling. Cal/EPA prefers that all sampling equipment be dedicated to a particular well. To encourage innovation, Cal/EPA may allow the use of other devices that are not specifically mentioned above if the RP demonstrates that the device will yield representative ground-water samples.

The following requirements should apply to the selection of sampling equipment:

- Sampling equipment should be chosen based on the analytes of interest and the characteristics and depth of the saturated zone from which the sample is withdrawn. For example, the choice of sampling equipment should reflect consideration of the potential for LNAPLs and DNAPLs.

- Sampling equipment should be constructed of inert material. Sample collection equipment should not alter analyte concentrations, cause loss of analytes via sorption, or cause gain of analytes via desorption, degradation, or corrosion.

- Sampling equipment should cause minimal sample agitation and should be selected to reduce/eliminate sample contact with the atmosphere during sample transfer. Sampling equipment should not allow volatilization or aeration of samples to the extent that analyte concentrations are altered.

The following sections discuss each category and type of available sampling device, including their appropriateness for use and their relative advantages and disadvantages.

2.3.1 Grab Samplers

There are two types of grab samplers available: bailers and syringe devices.

<u>Bailers</u>

Bailers are among the simplest ground-water sampling devices. A bailer is simply a rigid tube that fills with water when lowered into the well; when raised back out

Table 1. Generalized guide for selection of ground water sampling devices. From USEPA (1991).

		Device	Approximate Maximum Sample Depth	Minimum Well Diameter	Sample Delivery Rate or Volume†	GROUND-WATER PARAMETERS: INORGANIC: EC	INORGANIC: pH	INORGANIC: Redox	INORGANIC: Major Ions	INORGANIC: Trace metals	INORGANIC: Nitrate Fluoride	INORGANIC: Dissolved gasses	ORGANIC: Non-volatile	ORGANIC: Volatile	ORGANIC: TOC	ORGANIC: TOX	RADIO-ACTIVE: Radium	RADIO-ACTIVE: Gross alpha & beta	BIOLOGICAL: Coliform bacteria
PORTABLE SAMPLING DEVICES	GRAB	Open Bailer	no limit	1/2 in.	variable	●	¤	¤	●	●	●	¤	●	¤	¤	¤	●	¤	●
PORTABLE SAMPLING DEVICES	GRAB	Point-Source Bailer	no limit	1/2 in.	variable	●	●	●	●	●	●	¤	●	¤	●	●	●	¤	●
PORTABLE SAMPLING DEVICES	GRAB	Syringe sampler	no limit	1 1/2 in.	0.01-0.2 gal	●	●	●	●	●	●	¤	●	●	¤	¤	●	●	●
PORTABLE SAMPLING DEVICES	POSITIVE DISPLACEMENT (SUBMERSIBLE)	Gear-drive	200 ft.	2 in.	0-0.5 gpm	●	●	●	●	●	●	●	●	●	●	●	●	●	¤
PORTABLE SAMPLING DEVICES	POSITIVE DISPLACEMENT (SUBMERSIBLE)	Bladder pump	400 ft.	1 1/2 in.	0-2 gpm	●	●	●	●	●	●	●	●	●	●	●	●	●	●
PORTABLE SAMPLING DEVICES	POSITIVE DISPLACEMENT (SUBMERSIBLE)	Helical rotor	160 ft.	2 in.	0-1.2 gpm	●	●	●	●	●	●	●	●	●	●	●	●	●	¤
PORTABLE SAMPLING DEVICES	POSITIVE DISPLACEMENT (SUBMERSIBLE)	Piston pump (gas-drive)	500 ft.	1 1/2 in.	0-0.5 gpm	●	¤	¤	●	●	●	¤	●	●	¤	¤	●	●	¤
PORTABLE SAMPLING DEVICES	POSITIVE DISPLACEMENT (SUBMERSIBLE)	Centrifugal (Low-rate)	variable	2 in.	variable	●	●	●	●	●	●	●	●	●	●	●	●	●	●
PORTABLE SAMPLING DEVICES	SUCTION LIFT	Peristaltic	26 ft.	1/2 in.	0.01-0 3 gpm	●	¤	¤	●	●	●	¤	●	¤	¤	¤	●	¤	●
PORTABLE SAMPLING DEVICES	GAS CONTACT	Gas-lift	variable	1 in.	variable	¤	¤	¤	¤	¤	¤	¤	¤	¤	¤	¤	¤	¤	¤
PORTABLE SAMPLING DEVICES	GAS CONTACT	Gas-drive	150 ft.	1 in.	0.2 gpm	●	¤	¤	●	¤	●	¤	●	¤	¤	¤	●	¤	¤
IN SITU SAMPLING DEVICES*		Pneumatic	no limit	no limit	0.01-0.13 gpm	●	●	●	●	●	●	¤	●	¤	¤	¤	●	●	●

Sampling devices on this chart are divided into two categories: 1. portable devices for sampling existing monitoring wells, and 2. In situ monitoring devices (often multilevel) that are permanently intalled. Sampling device construction materials (including tubing, haul lines, etc.) should be evaluated for suitability in analyzing specific ground-water parameters. It is assumed on this chart that existing monitoring wells are properly installed and constructed of materials suitable for detection of the parameters of interest.

t Sample delivery rates and volumes are average ranges based on typical field conditions. Actual delivery rates area function of diameter of monitoring well, size and capacity of sampling device, hydrogeologic conditions, and depth to sampling point. For all devices, delivery rate should be carefully controlled to prevent aeration or degassing of the sample.

• Indicates device is generally suitable for application (assuming device is cleaned and operated properly and is constructed or suitable materials).

¤ Indicates device may be unsuitable or is untested for application.

Source: Modified from Pohlmann and Hess, 1988

Based on Literature Review

of the well, it is sealed on one or both ends by some mechanism. The ground-water sample is subsequently transferred into sample containers from the bailer. Bailers are relatively inexpensive to purchase or fabricate (especially the single and double check valve bailers), easy to clean, portable, simple to operate, and require no external power source (U.S. EPA, **1983).** Disadvantages are that their use can be time consuming and labor intensive and that the transfer of water to a sample container may significantly alter the chemistry of ground-water samples due to degassing, volatilization or aeration. Use of a bailer may also result in an increase of turbidity that may affect analysis results. The four main varieties of bailers are the single check valve, double check valve, messenger, and syringe bailers.

Recent research focusing on the comparison of different types of ground-water sampling equipment demonstrates that significant loss of volatile organic compounds may occur when bailers are used to sample ground water (Pearsall and Eckhardt, **1987;** Yeskis et al., **1988;** Tai et al., **1991).** Bailers should not be used to sample ground water that will be analyzed for volatile organic compounds, unless a bailer is the only available method for sampling an LNAPL or DNAPL or the use of a bailer is approved by the lead regulatory agency.

Bailers used to collect ground-water samples for inorganic analyses should be constructed of either fluorocarbon resin or PVC. Bailers used to collect ground-water samples for organic analyses should be constructed of stainless steel. The cable used to raise and lower the bailer should also be an inert material or coated with an inert material. Ideally the bailer should be easy to disassemble to facilitate cleaning and decontamination.

Bailers should never be dropped into a well and should be removed from the well in a manner that causes as little agitation to the sample as possible. For example, the bailer should not be removed in a jerky fashion or be allowed to continually bang against the well casing as it is drawn u. To eensure consistent samples, Cal/EPA recommends that the bailer be submerged only to a depth necessary for filling, except when the bailer is being used to sample a DNAPL. When transferring the sample from a bailer to a container, it is preferable to use a bottom emptying device with a valve to allow the water to slowly drain from the bailer. The sample should be allowed to run down the sides of the collection bottle to avoid excessive agitation of the sample.

Single Check Valve Bailers

A single check valve bailer has a check valve at the bottom of the sample chamber to seal the bailer when it is withdrawn from a well. A ball and seat arrangement is most common. In operation, the single check valve bailer is slowly lowered into the well annulus, water enters the chamber through the bottom, and when the bailer is withdrawn, the ball immediately seats with little or no sample loss through the check valve. Single check valve bailers provide a portable and simple means for collecting a water sample. Limitations include: difficulty in ascertaining the point the sample represents within the water column, oxidation near the sample surface, and possible disturbance of the water column by the sampler. Single check valve bailers should not be used if the well has been purged by withdrawing water from the top or center of the well screen because the bailer may sample stagnant water located above the screened interval as it is raised through the water column.

Double Check Valve Bailers

The double check valve bailer (also known as the point source bailer) is designed for sampling a prescribed depth within a water column. In this design, water flows through the sample chamber as the bailer is lowered. A tapered inlet and outlet ensures that water passes freely through the bailer with minimum disturbance to the water column. When the desired depth is reached, the bailer is retrieved. Because the tolerance between each ball and check valve seat is maintained by a pin that blocks the vertical movement of the check ball, both check valves close simultaneously upon retrieval. A bottom-emptying device is placed into the bottom of the bailer to discharge the sample. The device minimizes agitation and allows the sample to flow slowly into the sample container. Inert tubing may also be attached to the bottom emptying device and connected to a two way stoppered bottle into which the nonaerated sample flows. Double check valve bailers provide a means for collecting a relatively undisturbed water sample within a water column.

Syringe Bailer

A syringe bailer is distinguished from other bailers by the means of water entry (Morrison, 1983). The syringe is lowered into a well and water is drawn into the chamber by activating a plunger via suction. To recover the sample, the syringe is withdrawn from the well and the sample is transferred into a collection bottle or injected directly into an appropriate instrument for water quality analysis. The syringe bailer is a good sampling method when used as both a sampler and a sample container. The advantages of this approach include the ability to collect point source samples and the ability to collect samples for volatile organic analysis. The small syringe size is a limitation when large sample volumes are required.

2.3.2 Positive Displacement (Submersible) Mechanism

Positive displacement mechanisms for ground-water sampling include gear drive electric submersible pumps, bladder pumps, helical rotor electric submersible pumps, gas-drive piston pumps, and centrifugal pumps. The following sections describe each of these types of pumps and their applications and limitations with regard to collecting ground-water samples.

Bladder Pumps

Bladder pumps (also referred to as gas squeeze pumps) consist of a flexible membrane often enclosed in a rigid stainless steel housing. A strainer or screen attaches below the bladder to filter any material that could clog either of the check valves located above and below the bladder. Water enters the membrane through the lower check valve; compressed gas is injected into the cavity between the housing and bladder. The sample is transported through the upper check valve and into the discharge line. The upper check valve prevents water from reentering the bladder. The process is repeated to cycle the water to the surface. Bladder volumes (e.g., volume per cycle) and sampler geometry can be modified to increase the sampling abilities of the pump. Automated control systems are available to control gas flow rates and pressurization cycles. Bladder pumps prevent contact between the gas and water sample and can be fabricated entirely of fluorocarbon resin and stainless steel. A nearly continuous flow can be attained with the proper cycles. Pumps of this type can be used to sample wells greater than or equal to ***5*** cm (2 in) in diameter (Gillham et al., 1983). Pohlmann and Hess (1988) determined that bladder pumps can be suitable for collecting ground-water samples for almost any given organic or inorganic constituent. Disadvantages of bladder pumps include the large gas volumes required to actuate the pump (especially for sampling deep ground water), and potential bladder rupture.

If a bladder pump has been chosen as the sampling device, it should be operated at a discharge rate of 100 ml/min or less when collecting samples for volatiles analysis. Higher flow rates can increase the loss of volatile constituents and can cause fluctuation in pH and pH-sensitive analytes. Bladder pumps should be operated in a continuous, non-pulsating manner so that they do not produce samples that are aerated in the return tube or upon discharge. Once the portions of the sample reserved for the analysis of volatile components have been collected, a higher pumping rate may be used, particularly if a large sample volume will be collected. The pump lines should be cleared at a low rate before collecting samples for volatiles analysis, or else the sample collected will be from when the pump was rapidly operating. Running the pump at a low flow rate will take time and may deter the use of a bladder pump when the wells are deep and the lines are long.

Helical Rotor Electric Submersible Pumps

The helical rotor electric submersible pump consists of a sealed electric motor that powers a helical rotor. The water sample is forced up a discharge line by an electrically driven rotor-stator assembly by centrifugal action. Submersible pumps provide relatively high discharge rates for water withdrawal at depths beyond suction lift capabilities. Pumping rates vary depending upon the size of the motor and sampling depth. A submersible pump provides higher extraction rates than the majority of other methods. However, considerable sample agitation in the well results from operating at high rates, and this may cause alteration of the sample chemistry. In addition, high pumping rates can introduce sediments from the formation into the well that are immobile under ambient ground-water flow conditions, resulting in the collection of unrepresentative samples. Further, the potential exists for the introduction of trace metals into the sample from the pump materials. Steam cleaning of the unit followed by rinsing with unchlorinated, deionized water in between sampling is recommended. Where the submersible pump is used for sampling, those parts of the pump in contact with water should be constructed of stainless steel.

Gas-drive Piston Pumps

A piston pump uses compressed air to force a piston to raise the sample to the surface. A typical design consists of a stainless steel chamber between two pistons. The alternating chamber pressurization activates the piston, which allows water entry during the suction stroke of the piston, and forces the sample to the surface during the pressure stroke. Pumping rates of **500** mllmin have been reported from **30.5** meters; sampling depths of **150** meters are possible. The piston pump provides continuous sample withdrawal at depths greater than is possible with most other approaches. Nevertheless, contribution of trace elements from the stainless steel and brass fittings is a potential problem. Pumping rates at depths less than **150** meters are generally slower than with other pumps.

Centrifugal Pumps

A centrifugal (sometimes called impeller) pump is similar to **the** direct line pump except that a centrifugal pump is connected to the tubing at the surface rather than a vacuum pump. A foot valve is usually attached to the end of the well tubing to assist in priming the extraction tube. A centrifugal pump is capable of delivering large quantities of water, against high as well as low head conditions, with good efficiency. Under field conditions a centrifugal pump has an average suction lift capability of 20-25 feet **(6.1-7.6** meters) (Driscoll, **1986).** Although relatively high pumping rates can be attained, centrifugal pumps cause sample agitation.

2.3.3 Suction Lift Pumps

Suction lift pumps can be categorized **as** direct line and peristaltic. The direct line pump requires lowering one end of a plastic tube into a well or piezometer. The surface end of the tube is connected to a two-way stoppered bottle, and a manually or auxiliary powered vacuum pump is attached to a second tube that leads from the bottle. A check valve is attached between the second tube and the vacuum pump to maintain a constant vacuum control.

A peristaltic pump (also called rotary peristaltic) is a self-priming, low-volume suction pump consisting of a rotor and three ball bearing rollers. Plastic tubing inserted around the pump rotor is squeezed by the rollers as they revolve in a circle around the rotor. One end of the tubing is placed into the well while the other end is connected directly to a two-way stoppered flask. As the rotor revolves, water is drawn into the sampling tube and discharged into the collection vessel. A drive shaft connected to the rotor head can be extended so that multiple rotor heads can be attached to a single drive shaft. The withdrawal rate of peristaltic pumps can be carefully regulated by adjusting the rotor head revolution. The system can be arranged so that the sample contacts only fluorocarbon resin tubing prior to entering the sample container. A limiting factor is the depth of sampling; the depth of sample collection is limited to situations where the potentiometric level is less than 25 feet below land surface (Nielsen, **1991).**

The suction lift approach offers a simple retrieval method for shallow monitoring wells. However, the method can result in sample mixing and oxidation. Degassing and loss of volatiles also occur to some extent. A peristaltic pump provides a lower sampling rate and less agitation than direct line or centrifugal pumps.

2.3.4 Gas Contact Pumps

Gas contact sampling devices include gas-lift and gas-drive devices.

Gas-Lift Pumps

An air or gas lift pump allows collection of ground-water samples by bubbling air or gas at depth in the well. Sample transport occurs primarily as a result of the reduced specific gravity of the water being lifted to the surface. Water is forced up a discharge pipe, which may be the outer casing or a smaller diameter pipe inserted into the well. Air or gas lift methods can result in considerable sample agitation and mixing in the well, and are not permitted for collecting samples for chemical analysis. The considerable pressures required for deep sampling can result in significant redox and pH changes.

Gas-Drive Pumps

Gas drive (gas displacement) pumps are distinguished from air lift pumps by their method of sample transport. Gas displacement pumps force a column of water under linear flow conditions to the surface without extensive mixing of the pressurized gas and water. A vacuum can also be used to assist the gas. The disadvantages of a gas drive pump are that the drive gas comes into contact with the water and therefore, can be a source of contamination; also, the pump can be difficult to clean.

2.3.5 Packer Assemblages

A packer assembly provides a means by which to isolate and sample a discrete interval in the subsurface. Hydraulic- or pneumatic-activated packers are wedged against the casing wall or screen allowing sample collection from an isolated portion of the well. The packers deflate for vertical movement within the well and inflate when the desired depth is attained. Packers are usually constructed from some type of rubber or rubber compound and can be used with submersible, gas lift, and suction pumps.

If pumps are operated at a low rate, a packer assembly allows sampling of low-yielding wells, and wells that would otherwise produce turbid samples. **A** number of different samplers can be placed within the packers depending upon the analytical specifications for sample testing. One disadvantage is that vertical movement of water outside the well is possible with packer assemblages, depending upon the pumping rate and formation properties. Another possible disadvantage is that the packer material may contribute undesirable organic constituents to the water sample.

2.3.6 Decontaminating Sampling Equipment

When dedicated equipment is not used for sampling (or purging), or when dedicated equipment is stored outside of the well, the SAP should include procedures for disassembly and cleaning of equipment before each use at each well.

The recommended cleaning procedure when organic constituents are of interest is as follows: wash the equipment with a nonphosphate detergent and rinse with tap water, reagent grade acetone, and organic-free reagent water, in that order. If acetone is an analyte of interest, a different solvent (that is not a target analyte) should be chosen (e.g., isopropanol). The recommended cleaning procedure for inorganic constituents of interest is as follows: wash the equipment with a nonphosphate detergent/soap mixture and rinse with dilute (0.1M) hydrochloric or nitric acid, tap water, and reagent water, in that order. Dilute hydrochloric acid with a reagent water rinse is preferred when cleaning stainless steel because nitric acid may oxidize the steel. The waste decontamination fluids should be containerized and characterized to determine whether they should be treated or disposed of as hazardous waste.

All equipment should be allowed to dry thoroughly in a dust-free environment. If the equipment is not to be used again immediately, it should be packaged and properly stored to protect it from dust and dirt. Equipment may be wrapped in aluminum foil (shiny side on the outside) and placed in a plastic bag. A label should be affied to the outside wrapping stating the type of decontamination used and the date of decontamination. Clean sampling equipment should not be placed on the ground or on other contaminated surfaces prior to insertion in the well.

2.3.7 Collecting Ground-Water Samples

Monitoring well sampling should always progress from the well expected to be least contaminated to the well expected to be most contaminated, to minimize the potential for cross-contamination of samples that may result from inadequate decontamination of sampling equipment. Samples should be collected and containerized according to the volatility of the target analytes. The preferred collection order for some of the more common ground-water analytes is as follows:

- Volatile organics (VOAs or VOCs);
- Semivolatile organics (SMVs or SVOCs);
- Major water quality cations and anions;
- Stable isotopes (e.g. oxygen, hydrogen, nitrogen, lead)
- Metals;
- Cyanide;

- Turbitiy; and
- Radionuclides.

The following requirements should apply to the use and operation of ground-water sampling equipment:

- Check valves should be designed and inspected to ensure that fouling problems do not reduce delivery capabilities or result in aeration of samples.
- Sampling equipment (especially bailers) should never be dropped into the well, as this will cause degassing of the water upon impact.
- Sampler contents should be transferred to sample containers in a way that will minimize sample agitation and aeration.
- Clean sampling equipment should not be allowed to come into contact with the ground or other contaminated surfaces prior to insertion into the well.
- The rate at which a well is sampled should not exceed the rate at which the well was purged. Low sampling rates (less than 1 L/min) are suggested for wells that have historically yielded turbid samples (Puls et al., 1991). Rates as low as 100 to 500 mL/min have been successfully used to sample wells (Puls, et al., 1990; Puls and Barcelona, 1989a).

2.4 In-Situ or Field Analyses

Physically or chemically unstable analytes should be measured in the field, rather than in the laboratory. Examples of unstable parameters include pH, redox potential, chlorine, dissolved oxygen, and temperature. It is suggested that dissolved oxygen, turbidity, and specific conductance be determined in the field as soon as practicable. Although the specific conductance (i.e., electrical conductance) of a sample should be relatively stable, Cal/EPA recommends that this analyte also be measured in the field. Most conductivity instruments require temperature compensation; therefore, the temperature of the samples should be measured at the time conductivity is determined unless the monitoring equipment automatically makes this compensation.

Three methods can be employed for measuring unstable field parameters. One method is to use specially designed meters that have probes that may be lowered down into the well. The second method is to use an in-line flow-through monitoring chamber with ports for probe attachment, allowing continuous readings during purging. The third method is to collect a sample in a clean bottle or beaker in the same manner that a sample for laboratory analysis would be collected, and then to analyze the sample using a field test kit or meter. Unstable parameters should be measured in samples collected from the well after the well has been purged and before samples are collected for laboratory analysis. If down-hole probes (pH electrode, specific ion electrode, thermistor) are used to measure unstable parameters, the probes should be decontaminated in a manner that prevents the probe(s) from contaminating the water in the well. In no case should field analyses be performed directly on samples that will be submitted for laboratory analysis. Monitoring probes should not be placed in shipping containers containing ground-water samples for laboratory analysis.

The SAP should list the specific parameters that will be measured in the field. The program should specify the types of instruments (e.g., downhole probes, meters) that will be used to make these measurements, and describe the procedures that will be followed in operating the instruments and recording the measurements. The SAP should describe all instrument calibration procedures, including the frequency of calibration. The description of calibration procedures should include: discussion of initial calibration, multi-level calibration for determination of usable range, periodic calibration checks, conditions that warrant re-calibration of instruments, acceptable control limits, and the maintenance of calibration records in the field log book. At a minimum, all field instruments should be calibrated at the beginning of each use and in accordance with the frequency suggested by the manufacturer. Field instruments should be calibrated using at least two calibration standards spanning the range of results anticipated during the sampling event. For example, if ground-water pH is expected to be near pH 7, the two standards used to calibrate the pH meter should be pH 4 or 5, and pH 9 or 10, respectively.

2.5 Sample Preservation and Handling

The procedures employed for sample preservation and handling are nearly as important for ensuring the integrity of the samples as the collection device itself. Table 2 may be used for guidance on containers and sample preservation. Detailed procedures for containerization, preservation, packaging, and handling (e.g., shipped daily by overnight courier) should be provided in the SAP. Samples collected from a well should never be composited in a large container for subsequent transfer to the appropriate smaller bottles. Regardless of the analytes of concern, exposure of the samples to the ambient air should be minimized.

Splitting of samples is commonly done. When sampling for volatile organic aromatic compounds (VOAs), the procedure is changed slightly. Normally, one half of the sample is emptied from the sampling device into one container, and one half is emptied into the other, with the procedure being repeated with each bailer until the containers are full. For VOAs, however, the first VOA container should be completely filled and sealed, and then the VOA container into which the other split sample will be placed should be completely filled and sealed.

2.5.1 Sample Containers

The SAP should identify the type of sample containers to be used to collect samples, as well as the procedures the RP will use to ensure that sample containers are free of contaminants prior to use. Refer to Table 2 for a list of appropriate sample containers, by analyte.

When metals are the analytes of interest, glass or polyethylene containers with polypropylene caps should be used. While polyethylene containers are acceptable

Table 2. Sampling and preservation requirements for ground-water samples

Parameter	Container	Preservation	Holding Time	No. of Samples & Minimum Volume (ml)
Acidity	P,G	Cool, 4" C	14 days	100
Alkalinity	P,G	Cool, 4" C	14 days	100
Ammonia	P,G	Cool, 4" C H_2SO_4 to pH < 2	28 days	1000
Asbestos	P	Cool, 4" C	48 hours	1000
PH	P,G	Determine on site	2 hours	50
Radioactivity	P,G	HNO_3, to pH < 2	6 months	1 gallon
TOX	Amber G-V	Cool, 4" C 1 mlO.l M Na_2SO_4, HNO_3, to pH < 2	7 days	3 x 100
TOC	P,G	Cool, 4" C	28 days	100
Chloride	P,G	None	28 days	100
Cyanide	P,G	NaOH to pH > 12	14 days	1000
Fluoride	P,G	None	28 days	500
Nitrate	P,G	Cool, 4" C	48 hours	500
Oxygen ($^{18}O/^{16}O$)	P,G,G-V	None	6 months	40
Hydrogen ($^2H/^3H$)	P,G,G-V	None	6 months	40
Nitrogen ($^{15}N/^{14}N$)	P,G	Cool, 4° C	28 days	1000
Sulfate	P,G	Cool, 4" C	28 days	200
Sulfide	P.G	Cool, 4" C 2 ml zinc acetate NaOH to pH > 9	7 days	1000
Chromium VI	P,G	Cool, 4" C	24 hours	500
Dissolved Metals (except Cr VI)	P,G	Filter on site HNO, to pH < 2	6 months (except Hg - 28 days)	1000
Total Metals	P,G	HNO_3, to pH < 2	6 months (except Hg - 28 days)	1000
Extractable Organics (EPA 8270)	G	Cool, 4" C	7 days to extraction, analysis 40 days after extraction	1000

Parameter	Container	Preservation	Holding Time	No. of Samples & Minimum Volume (ml)
Purgeable Organics (EPA 8260)	G-V	Cool, 4" C H_2S0_4, HCl or NaHSO, topH < 2	14 days	2 x 40
Purgeable Aromatics	G-V	Cool, 4" C H_2S0_4, Hcl or NaHSO, to pH < 2	14 days	2 x 40
Acrolein & Acrylonitrile	G-V	Cool, 4" C Adjust pH to 4-5	14 days	2 x 40
Gasoline	G-V	Cool, 4" C H_2SO_4, Hcl or NaHSO, topH<2	14 days	2 x 40
Pesticides & PCBs	*G*	Cool, 4" C	7 days to extraction, analysis 40 days after extraction	1000
Phenols	G	Cool, 4" C	7 days to extraction, analysis 40 days after extraction	1000
Oil & Grease	G	Cool, 4° C H_2SO_4 to pH < 2	28 days	1000

a: P = Polyethylene container with polypropylene closure.
G = Glass container with Teflon-lined closure.
G-V = Glass VOA vial or bottle with Teflon septum.

for holding samples that will be analyzed for metals, Cal/EPA recommends the use of glass containers instead. There is evidence that metals may sorb into the polyethylene matrix and that the acid preservative may fail to desorb them. When organics are the analytes of interest, glass bottles with Teflon-lined caps should be used. The SAP should refer to the specific analytical method that designates an acceptable container.

New containers should be prepared based on the analyte of interest; used containers are to be discarded. The cleaning procedures used for sample containers are the same as those discussed in Section **2.3.6.** The cleanliness of a batch of precleaned bottles should be verified in the laboratory. The residue analysis should be available prior to sampling in the field.

2.5.2 Sample Preservation

The SAP should identify the sample preservation methods that will be used. Methods of sample preservation are relatively limited, and are generally intended to **1)** retard biological action, **2)** retard chemical reactions such as hydrolysis or oxidation, and 3) reduce sorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration, and protection from light.

Most sample containers provided by a laboratory have pre-added preservative. If these are not available, then preservatives should be added in the field. No sample should be brought back to the laboratory for preservation. For pH control, test strips should be used to verify that samples have attained the appropriate pH range for sample preservation.

Most commercial shipping containers ("coolers") leak when the interior water level reaches the lid-body interface. As a result, the carrier may refuse to ship the container. For this reason, Cal/EPA recommends that two polyethylene overpack bags be used in shipping. The first will contain the sample bottles, the second the ice needed to keep the samples at **4°C.** If the bags are taped shut, the melt water will not reach the bottle labels or escape from the cooler. This precaution may not be necessary if "blue" ice or other contained coolants are used. Glass containers should be protected from breakage using bubble wrap and/or vermiculite. The vermiculite will also absorb any spills or melted ice.

As specified by U.S. EPA **(1986),** a temperature history of the samples should be maintained as a quality control measure. This is done by recording the temperature on the chain-of-custody record (Section **2.6)** before the sample containers are sealed for shipment. Upon receipt of the shipment, the laboratory is required to record the temperature at receipt on the chain-of-custody record.

Holding time refers to the period that begins when the sample is collected from the well and ends with its extraction or analysis. Holding time is not measured from the time the laboratory receives the samples. Any laboratory submission to Cal/EPA should contain the date/time sampled, the date/time received, the date/time extracted, and the date/time analyzed.

2.5.3 Specia Handling Considerations

During ground-water sampling, every attempt should be made to minimize changes in the chemistry of the samples so that data representative of subsurface hydrogeochemistry are collected. Cal/EPA agrees with the following U.S. EPA protocols that will assist in preserving the natural chemistry of ground-water samples: 1) do not routinely filter ground-water samples in the field, 2) do not transfer samples from one sample container to another, and 3) do not allow headspace in the containers of samples that will be analyzed for volatile organics.

Ground-water samples used to determine if there is statistically significant evidence of ground-water contamination by organic compounds should not be field-filtered. Data generated from filtered samples provide information on only the dissolved constituents that are present, as suspended materials are removed by the filtration process. The analytical results of these ground-water samples are used to determine if a facility is releasing hazardous constituents to ground-water. As discussed in greater detail below, current research in ground-water sampling protocol indicates that hazardous constituents are mobile in the subsurface in both the aqueous (dissolved) phase and the solid phase. The research of Puls and Barcelona (1989a), Puls and Barcelona (1989b), Penrose et al. (1990), and West (1990) are the primary sources of the discussion of field filtration that follows.

During ground-water sampling, every attempt should be made to minimize changes in the chemistry of the sample so that data representative of hazardous constituents that may be migrating to ground-water can be collected. A sample that is exposed to the atmosphere as a result of field filtering is very likely to undergo chemical reactions (e.g., volatilization, precipitation, chemical flocculation) that alter constituent concentrations. These reactions can change the concentrations of organic compounds and metals if they are present in the sample. Volatile organic compounds **(VOCs)** are likely to partition to the atmosphere if exposed, thereby resulting in ground-water monitoring data that are not representative of constituent concentrations. Further, precipitated and emulsion trapped constituents migrating from the facility to ground-water are lost through field filtering, because they are unable to pass through a standard **0.45** micron field filter.

For metals analysis of ground-water samples, however, the situation is not as clear. The argument against filtering is that it will not provide accurate information concerning the mobility of metal contaminants. Some metals may move through fractured, karstic, and porous media not only as dissolved species, but also as precipitated phases, and/or polymeric species; some metals may be adsorbed to, or encapsulated in, organic or inorganic particles (e.g., colloid-size particles), that are likely to be removed by filtration. In addition, field filtration may introduce oxygen into the sample, which can oxidize dissolved ferrous iron to form a ferric hydroxide precipitate ($Fe(OH_3)$,);this may enmesh other metals in the sample, removing them from solution. The precipitate and the entrapped constituents would be removed by field filtration.

The argument for filtering samples (prior to analysis for inorganic constituents) is that small differences in sample turbidity can mean very large differences in analytical results. Sample turbidity is an indirect measurement of the amount of particulate matter suspended in a sample, and is highly dependent on the nature of the aquifer material. In aquifers containing significant silt or clay, turbidity can be reduced through proper well design, construction and development, and by use of appropriate sample collection methods, However, turbidity is rarely eliminated. Since sample turbidity is not directly related to sources of contamination, resulting values from unfiltered samples do not necessarily provide direct evidence of metals contamination, and are generally not a useful indication of contaminant load in an aquifer.

Based on these arguments, the following recommendations are provided **as** a guide to sampling ground water for the analysis of trace metals:

- Filtered samples for dissolved metals analysis should be used whenever ground-water samples are collected to determine if water quality has been affected by a hazardous substance release that includes metals as a constituent of concern;
- Samples should never be filtered when a water supply well is sampled;
- For risk assessment, unfiltered samples should also be considered if the hydrogeologist suspects that colloidal transport in the aquifer could be significant (i.e,, in karst or fracture-dominated aquifers); it is also recommended that filtered samples be collected at the same time for comparison.

Since significant differences in water quality may be attributed to contamination, it is critical to control other variables that may affect ground-water quality. In addition to factors already discussed in this document, these recommendations, where applicable, should also be followed:

- Monitoring wells should be designed, constructed and developed to minimize turbidity; well construction is discussed in <u>Monitoring Well Design and Construction for HydrgeologicCharacterization</u> **(Cal/EPA,** 1995);
- Whenever possible, well purging and sampling should be performed with dedicated, low-flow pumps;
- Wells should be purged until measured values for temperature, pH and specific conductance are stable;
- In-line, positive-pressure filters should be used at all times--vacuum filtration is not acceptable;
- Manufacturer's recommendations for the volume of water to be flushed through the filter prior to sampling should be followed; if guidelines are not available, a volume of ground water equal to twice the capacity of the filter should be flushed through the filter and discarded before collecting samples.

There are certain circumstances where it is necessary to filter or centrifuge the sample under controlled laboratory conditions prior to analysis to prevent instrument damage. Sample filtration in the laboratory is permissible if insoluble materials that could damage laboratory equipment (e.g., silicates) remain after acid digestion of the sample. If this step is necessary, the filter and the filtering apparatus should be thoroughly cleaned and pre-rinsed with dilute nitric acid. Laboratory personnel should refer to **SW-846** **(U.S.** EPA, **1986)** for information concerning these procedures.

Samples should not be transferred from one sample container to another. Transferring samples between containers may result in losses of organic material onto the walls of the container or sample aeration.

To minimize the possibility of volatilization of organics, no headspace should exist in the containers of samples containing volatile organics. Field logs and laboratory analysis reports should note the headspace, if present, in the sample container(s) at the time of receipt by the laboratory, as well as at the time the sample was first transferred to the sample container at the wellhead.

2.6 Chain-of-Custody and Records Management

A chain-of-custody procedure should be designed to allow the RP to reconstruct how and under what circumstances a sample was collected, including any problems encountered. **U.S.** EPA **(1986)** provides a complete description of chain-of-custody and records management. The chain-of-custody procedure is intended to prevent misidentification of the samples, to prevent tampering with the samples during shipping and storage, to allow easy identification of any tampering, and to allow for the easy tracking of possession.

2.6.1 Sample Labels

To prevent sample misidentification, the RP should affix labels to each sample container. The labels should be sufficiently durable to remain legible even when wet and should contain, at a minimum, the following information:

- Sample identification number;
- Name and signature of collector;
- Date and time of collection;
- Place of collection; and
- Parameters requested (if space permits).

The samples can be labeled by recording the above information directly on the sample containers. Alternatively, the RP may use multiple-part labels consisting of a unique identification number that is placed on the container, and at least two copies of the descriptive information for the samples (referenced to the identification number). One copy should be kept in a separate file or logbook, and a second copy is shipped inside the cooler with the samples to the laboratory.

2.6.2 Sample Custody Seal

In cases where samples leave the RPs immediate control (shipment to laboratory, for example), a custody seal should be placed on the shipping container or on the individual sample bottles. Custody seals provide prevention or easy detection of sample tampering. The custody seal should bear the signature of the collector and the collection date. It can be placed on the front and back of a cooler, around the mouth of a polyethylene overpack bag or on the lid of each sample container before it is taped shut for shipping. Caution should be exercised in doing any of the above. Experience has shown that the seal may not always adhere to some plastic coolers, and the cooler may arrive at the destination without the appropriate seal. Sometimes the sample containers become wet from melting ice or condensation; thus, while their labels will stick, their custody seals may not. Taping over the seal with a transparent tape generally solves this problem. A similar solution can be applied to the cooler lids.

2.6.3 Field Logbook

If a sample analysis produces an unexpected or unexplainable result, it will be necessary to determine if the circumstances of sample collection, rather than a change in the ground-water quality, are responsible. Examination of the field logbook is critical in this process. The field logbook should document the following:

- Well identification;
- Condition of well and surface completion;
- Well depth;
- Static water level depth and measurement technique;
- Presence and thickness of immiscible layers and detection method;
- Well purging procedure and equipment;
- Purge volume and pumping rate;
- Time well purged;
- Well yield (high or low);
- Well recovery after purging (slow, fast);
- Collection method for immiscible layers;
- Sample withdrawal procedure and equipment;
- Date and time of collection;

- Well sampling sequence;
- Types of sample bottles used and sample identification numbers;
- Preservatives used and pH verification;
- Parameters requested for analysis;
- Field observations of sampling event;
- Name of collector;
- Climatic conditions, including air temperature; and
- Internal temperature of field and shipping containers.

2.6.4 Chain-of-Custody Record

The tracing of sample possession will be accomplished by use of a chain-of-custody record sheet. A chain-of-custody sheet should be filled out and should accompany every sample. It should also contain enough copies so that each person possessing the shipment receives his/her own copy. At a minimum, the record should contain the following information:

- Sample number;
- Signature of collector;
- Date and time of collection;
- Sample type (e.g., ground water);
- Identification of sampling point (well);
- Number and types of containers;
- Parameters requested for analysis;
- Preservatives used;
- Signature of persons involved in the chain of possession;
- Inclusive dates and times of possession;
- Internal temperature of shipping container when samples were sealed into the container for shipping;
- Internal temperature of container when opened at the laboratory; and

- Remarks section to identify potential hazards or to relay other information to the laboratory.

2.6.5 Sample Analysis Request Sheet

This document should accompany the sample(s) on delivery to the laboratory and clearly identify which sample containers have been designated for each requested parameter. It may be included in the chain-of-custody record. Addition of preservatives should also be noted. This document should include the following types of information:

- Name of person receiving the sample;
- Name and addresses of analytical laboratory;
- Laboratory sample number (if different from field number);
- Date of sample receipt;
- Analyses to be performed;
- Internal temperature of shipping container upon opening in the laboratory; and
- Preservatives added in the field.

2.6.6 Laboratory Logbook

Once the sample has been received in the laboratory, the sample custodian and/or laboratory personnel should clearly document the processing steps that are applied to the sample. All sample preparation techniques and instrumental methods used should be identified in the logbook. Experimental conditions, such as the use of specific reagents, temperatures, reaction times, and instrument settings, should be noted. The results of the analyses of all laboratory quality control samples should be identified, specific to each batch of ground-water samples analyzed. The laboratory logbook should include the time, date, and name of the person who performed each processing step.

2.7 Analytical Procedures

The ***SAP*** should describe in detail the analytical procedures that will be used to determine the concentrations of constituents or parameters of interest. These procedures should include suitable analytical methods as well as proper quality assurance and quality control protocols.

The ***SAP*** should identify a method that will be used for each specific parameter or target analyte that can achieve the required detection limits. The following should be addressed:

1. For **SW-846** analytical methods, reference **SW-846** and the analysis methods (by method number), including all sample preparation methods. For modified

SW-846, or other standard methods, the analytical procedure and method detection limits to be used should be documented in the format of a Standard Operating Procedure (SOP).

2. For analysis by non-SW-846 methods, the following should be provided:

   a) Approval of the U.S. EPA or Cal/EPA for standardized methods;

   b) For EPA or standardized methods, a reference to the source of the method; and

   c) For non-standard methods, a complete SOP, with method detection limit, should be included as an integrated part of the sampling and analysis program to be approved by the Cal/EPA and specified in the permit.

2.8 Field and Laboratory Quality Assurance/Quality Control

One of the fundamental responsibilities of the RP is the establishment of continuing programs to ensure the reliability and validity of field and analytical laboratory data gathered as part of the overall ground-water monitoring program. Refer to SW-846 (U.S. EPA, 1986) for requirements and guidance on establishing and maintaining field and laboratory quality control programs. In general, laboratory quality assurance and quality control (QA/QC) programs should address the following areas:

- Control samples;
- Acceptance criteria;
- Deviations;
- Corrective action for sampling and analysis procedures;
- Data handling;
- Laboratory control samples;
- Method blanks;
- Matrix-specific effects.

The **RPs' *SAP*** should explicitly describe the QA/QC program that will be used in the field and laboratory. The Data Quality Objectives (DQOs) of the project should be described in terms of precision, accuracy, completeness, representativeness and comparability for both field activities (sampling, measurements and screening) and laboratory analyses, including the project required acceptance limits and means to achieve these QA objectives. Refer to US EPA, QA/G-4 for a discussion of DQOs. In addition, the preventative maintenance procedures to be used for the field and laboratory instruments and the ground-water monitoring system should be described. A table showing the type of maintenance to be performed and the frequency is appropriate. Many RPs use commercial laboratories to conduct analyses of ground-water samples. In these cases, the SAP should be used by the laboratory analyzing samples for the RP.

Both field and laboratory QC samples should be prepared during the sampling event. The following samples should be analyzed with each batch of samples (a batch may not exceed 20 samples):

- One field blank suite;
- One equipment rinsate (required only when non-disposable equipment is being used);
- One matrix spike (when appropriate for the method); and
- One duplicate sample (either a matrix duplicate or a matrix spike duplicate).

In addition, a trip blank should be prepared and analyzed when samples are being analyzed for volatile organic analytes. A trip blank should be prepared for each day that samples are collected.

The matrix-specific detection limit should be determined. This determination does not need to be made on a sample batch basis, but should be made whenever the matrix is suspected to have altered, or as frequently as necessary to document that the matrix has not altered. For an aquifer with relatively static hydrogeological characteristics, this may mean making a matrix-specific detection limit determination twice annually.

2.8.1 Field QA/QC Program

The SAP should provide for the routine collection and analysis of QC samples. Various types of QC samples and blanks should be used to verify that the sample collection and handling process has not affected the quality of the samples. Blanks are to be subjected to the same analysis as the ground water. Contaminants found in the blanks may be the result of: (1) inter-action between the sample and the container, (2) contaminated rinse water, (3) contaminated preservatives, or (4) a handling procedure that alters the sample analysis results. The concentrations of any contaminants found in the blanks should not be used to correct the ground-water data. The contaminant concentrations should be noted, and if the concentrations are more than an order of magnitude greater than the field sample results, the RP should re-sample the ground water. All field QC samples should be prepared exactly as regular investigation samples with regard to sample volume, containers, and preservation. The RP should prepare the QC samples and analyze them for all of the required monitoring parameters.

Other QA/QC practices such as sampling equipment calibration and decontamination procedures and chain-of-custody procedures should be described in the SAP. Refer to the previous sections in this document for a discussion of these practices.

2.8.2 Laboratory QNQC Program

The SAP should provide for the use of control samples, as defined in SW-846 (U.S. EPA, 1986). The RP should use appropriate statistical procedures to monitor and document performance and to implement an effective program to resolve testing problems (e.g., instrument maintenance, operator training). Data from control samples (e.g., spiked samples, duplicates and blanks) should be used as a measure of performance or as an indicator of potential sources of cross-contamination. When contaminants are detected in QA/QC samples (field, trip, or lab blanks), the accompanying sample results should be appropriately flagged. All sample results shall be reported unadjusted for blank results or spike recoveries. All QA/QC data should be submitted to Cal/EPA with the ground-water monitoring sample results.

2.9 Evaluation of the Quality of Ground-Water Data

A ground-water sampling and analysis program produces a variety of hydrogeological, geophysical, and ground-water constituent concentration (GWCC) data. This section pertains primarily to the evaluation of GWCC data. The GWCC data may be presented to the owner or operator via electronic transmittal or on reporting sheets. These data then should be compiled and statistically analyzed by the RP prior to submittal to the lead regulatory agency. If data are to be transmitted electronically, the RP should discuss the procedures with the lead regulatory agency staff to ensure that all software and hardware being used are compatible.

The following guidelines should help to ensure that units of measure associated with data values are reported consistently and unambiguously:

- The units of measure should accompany each target analyte. Laboratory data sheets that include the statement "values are reported in ppm unless otherwise noted" should generally be discouraged, and at least should be examined in detail by the technical reviewer. It is common to find errors in reporting the units of measure on this type of data reporting sheet, especially when these reporting sheets have been prepared manually.

- The units of measure for a given target analyte should be consistent throughout the report.

RPs should ensure that during chemical analysis, laboratory reporting, computer automation, and report preparation, data are generated and processed to avoid mistakes, and that data are complete and fully documented. Data should be reported correctly for the results to be valid.

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COMMENT SHEET

As a user of this document, your comments are important. Please use this sheet to inform us of any errors, deficiencies or suggested improvements to this document. If you identify an error or deficiency, please suggest how it can be corrected. Attach additional sheets if necessary. Send your comments to:

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Name: **Address:**

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Title: Representative Sampling of Ground Water

Section:
Comment:

Suggested Revision:

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